# First Hyperpolarizability of 2, 5-Dimethyle Aniline by the Hyper Rayleigh Scattering Technique

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***Abstract:*** *The Hyper Rayleigh Scattering (HRS) technique has been used to obtain the first hyperpolarizability (β) of 2, 5-dimethyle aniline (DMA). The Methanol solution of DMA has been taken for the internal reference method of HRS. An Ar-ion laser operating at the wavelength of 457 nm has been used as the excitation source to generate the harmonic scattering of light. The incident laser power has been varied to obtain Second Harmonic Generation (SHG) at right angles to the incident direction.*

***Keywords:*** *2, 5-Dimethylaniline, Hyperpolarizability, Hyper-Rayleigh Scattering (HRS), Internal Reference Method, Isotropic Solutions, NLO Susceptibility, Second Harmonic Generation*

## I.    INTRODUCTION

Second harmonic generation from isotropic solution was first observed over three decades ago [1]. While coherent second harmonic generation (SHG) is cancelled    isotropic media due to symmetry [2], incoherent second harmonic scattering, known as hyper-Rayleigh scattering (HRS), is weakly allowed. Experimental techniques to measure the microscopic second-order nonlinear optical (NLO) polarizability β of a molecule have been complicated by the symmetry requirements for the observation of a macroscopic second-order NLO susceptibility β [3]. Second harmonic generation, the most widely used technique to measure the first hyper polarizability β, is forbidden in isotropic liquid [4]. Electric-field-induced second harmonic generation (EFISHG) makes the important advance that first hyperpolarizabilities can be measured directly in solution. The EFISHG technique measures a third-order nonlinearity from the coupling of the optical fields with the orienting dc field yielding, after suitable correction for local fields [3], a value for$+\frac{\beta\mu}{5KT}$ . Therefore, knowledge of the values of the dipole moment μ, the third order hyperpolarizability γ, and local field correction at zero frequency are required to extract the first hyperpolarizability β. The HRS popularity was revived when it was appreciated that HRS reports directly on the magnitude of the first hyperpolarizability tensor, β, of molecule in solution. β describes second order nonlinear optical (NLO) activity, an important characteristic of molecules designed for use in emerging technological applications such as photonics the photon based analog of electronics. In this article, we described the experimental setup and the procedure to obtain values for the first hyperpolarizability from the second- order light intensity.

## II.    THEORY

The induced dipole moment for a single molecule is, in Cartesian tensor notation,

$$\mu_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l \tag{1}$$

Here, $\mu_i$ is the component of the induced dipole moment along the molecule-fixed i axis, $\alpha_{ij}$ is the ij component of the polarizability tensor α, $\beta_{ijk}$ is the $ijk$ component of the microscopic (third-rank, second order) the first hyperpolarizability tensor β, $\gamma_{ijkl}$ is the ijkl component of the second hyperpolarizability tensor γ. $E_j$ is the electric field component along j axis.

The first order nonlinear polarizability of this model is given by [7],

$$\beta(\omega_1+\omega_1) = \frac{-2be(\frac{e}{m})^2}{(\omega_0{}^2-\omega_1{}^2-i\omega_1\gamma)(\omega_0{}^2-\omega_1{}^2\pm i\omega_1\gamma)} \tag{2}$$

A Hyper-Rayleigh scattering experiment is performed by measuring the intensity of the incoherently scattered frequency-doubled light generated by an intense laser beam from an isotropic solution [5, 6]. The scattered intensity of a single molecule can be calculated by,

$$I_{2\omega} = \frac{32\pi^2}{\epsilon_0^3\lambda^4r^2} < \beta_{HRS}^2 > I_\omega^2 \tag{3}$$

Where the brackets indicate the orientational averaging and r is the distance from to the scattered molecules.

The total intensity is proportional to the sum of the intensity scattered by the individual molecules:

$$I_{2\omega} = \frac{32\pi^2}{c\epsilon_0^3\lambda^4r^2} N(f_\omega)^4(f_{2\omega})^2 < \beta_{HRS}^2 > I_\omega^2 \tag{4}$$

Where N is the concentration of chromspheresand $f_\omega$, $f_{2\omega}$ are the local field factors .The most commonly used for isotropic solutions is the Lorentz correction factor,

$$f_\omega = \frac{n^2_{\omega+2}}{3} \tag{5}$$

Thus, the overall correction due to local fields is defined as:

$$f^2_\omega f_{2\omega} = F_L = \left[\left(\frac{n^2_\omega + 2}{3}\right)^2 (\frac{n^2_\omega + 2}{3})\right]$$

Then equation (4) can be simplified into:

$$I_{2\omega} = N G F_L^2 < \beta^2_{HRS} > I^2_\omega \tag{6}$$

In classical Hyper-Rayleigh Scattering experiments the $90^0$ angle geometry is mainly used. For a solution of two components (solvent and solute), the harmonic intensity $I_{2\omega}$ is given by (8):

$$I_{2\omega} = G(N_S < \beta^2_{HRS} >_S + N_X < \beta^2_{HRS} >_X)I^2_\omega = q.c.\times I^2_\omega \tag{7}$$

Where we have defined the quadratic coefficient:

$$q.c.\equiv G(N_S < \beta^2_{HRS} >_S + N_X < \beta^2_{HRS} >_X) \tag{8}$$

G includes all experimental factors and the subscript s and x refer to the solvent(s) and the chromophores(x).

### 2.1The Internal Reference Method

To take advantage of the linear dependence on the chromophores concentration $(Nx)$, a series of different concentrations are prepared. The quadratic coefficient for each concentration, $q. c.$ is then obtained. If$< \beta^2_{HRS} >_S$ is known and the experimental conditions are well characterized, $< \beta^2_{HRS} >_X$ can be obtained by calculating the slope of the quadratic coefficients as a function of concentration.
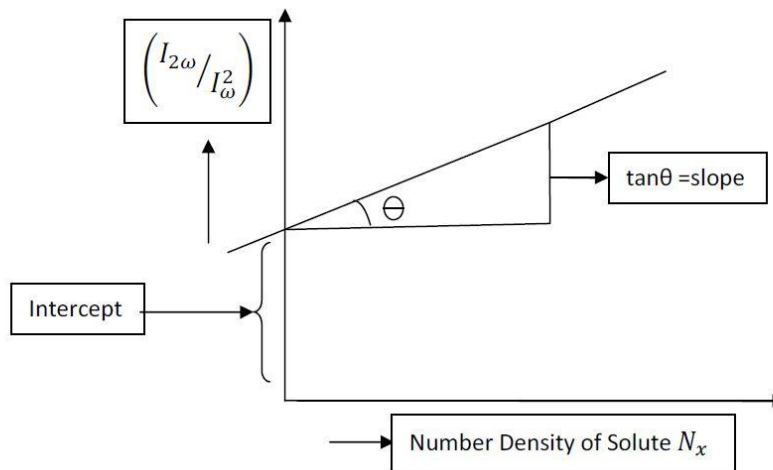


Figure 1: A schematic plot of $(\frac{I_{2\omega}}{I^2_\omega})$ vs. number density of solute $(Nx)$ showing the intercept and slope.

This is referred as the internal reference method. In the internal reference method a plot of the quadratic coefficients (q.c.) vs. as a function of $Nx$ yields a straight line with a slope $b_1$ and an intercept$b_0$. With the solvent value of$< \beta^2_{HRS} >_S$ known, this is used as an internal reference to determine that of the solute$< \beta^2_{HRS} >_X$. The working equation is given by:

$$< \beta^2_{HRS} >_X = \frac{b_1}{b_0} N_S < \beta^2_{HRS} >_S = \frac{b_1 N_A \rho_S}{b_0 M_S} < \beta^2_{HRS} >_S \tag{9}$$

### 2.2Experimental Setup

The fundamental light beam is passed through a beam splitter or grating scale that helps to split the beam in different wavelengths or different frequencies. Then we take the blue beam of wavelength 457nm. Then the blue beam is passed through the polarizer, half wave plate and focused in the cell by a convex lens. The collection system consists of a concave mirror, a convex lens and a power detector. In this experiment, first convex lens have focal length of 10 cm and in collection system 7.56 cm focal length convex lens are used. The concave mirror has a focal length 4.5 cm. We used power detector in place of photomultiplier. Because of this we found power P (2ω) of the scattered beam in place of intensity$I_{2\omega}$.
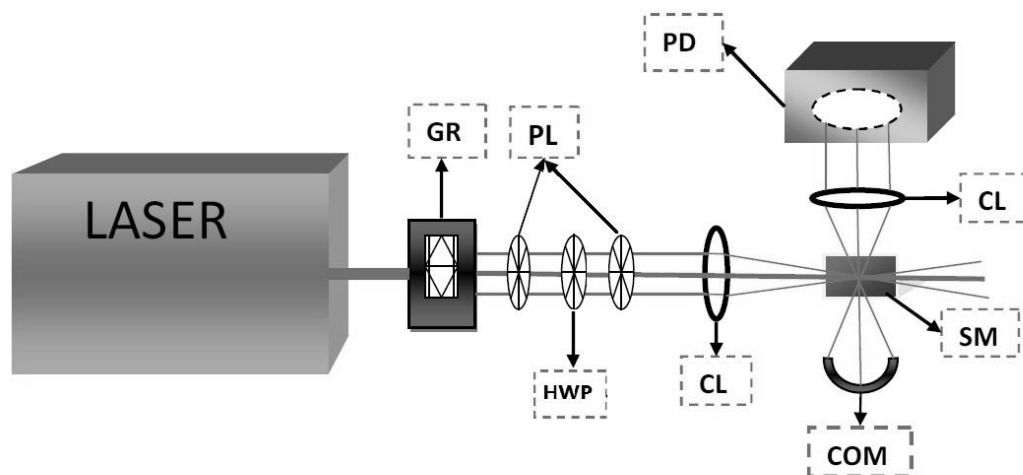
Figure 2: Schematic view of the experimental Hyper Rayleigh Scattering setup.
Where Grating (GR), Polarizer (PL), Half Wave Plate(HWP),  Convex Lens (CL), Concave
Mirror (COM), Power Detector(PD), Sample (SM).

### III.      SAMPLE PREPARATION
        **2, 5-**Dimethylaniline (DMA) is an http://en.wikipedia.org/wiki/Organic_compound" \o "Organic compound, a substituted derivative of aniline. It can be produced by well knownFridel-Craft alkylation reaction as following EMBED ChemDraw.Document.6.0
        Substitution of the aniline monomer with alkyl(-R) or alkoxy(-OR) groups improves then solubility in organic solvents such as methanol. Molecular weight of **2,5-**Dimethylaniline (DMA) is 121.18.Melting and boiling point of DMA are 11.5 °C(lit.) and 218 °C(lit.) respectively. Density of DMA is 0.973 g/mL at 25 °C(lit.). 2,5-Dimethylaniline may be sensitive to prolonged exposure to air and almost insoluble in water. 2, 5-Dimethylaniline ignites on contact with fuming nitric acid. It neutralizes acids in exothermic reactions to form salts plus water. May be incompatible with isocyanates, halogenated organics, peroxides, phenols (acidic), epoxides, anhydrides, and acid halides .It is combustible.
It is dark brown and very poor transparent liquid. Due to the low transparency of DMA, it was dissolved in methanol and three solution of DMA in methanol were made with the ratio (volume/volume) 1:15, 1:9 and 1:6.

### IV.      CALCULATION
        To determine the value of the First Hyper-Polarizibility of 2,5-Dimethyle, we use the internal reference method. In this method a plot of the quadratic coefficients (q.c.) plotted as a function of $Nx$ yields a straight line with a slope $b_1$ and an intercept $b_0$. With the known solvent value of $< \beta_{HRS}^2 >_S$, we are able to determine the solute $< \beta_{HRS}^2 >_X$.
For this at first we have to find the value of the quadratic coefficients (q.c.), which is the slope of $I_{2\omega} vs I_{\omega}^2$ graph. For each sample we have to find the value of the quadratic coefficients (q.c.).
Because of the power was measured in place of intensity so the equation $I2\omega = q.c. \times I_{\omega}^2$ is modified by:

$$\frac{P(2\omega)}{\Pi r_1^2} = q.c.\,(\frac{2P(\omega)}{\Pi r_2^2})^2 \qquad\qquad (10)$$

Where $r_1$is the radius of the detector which is 0.564 cm and $r_2$is the radius of the Gaussian laser beam which is 0.065 cm. The equation (10) is modified as

$$P(2\omega) = K \times q.c. \times P^2(\omega) \qquad\qquad (11)$$

We took 0.5ml 2, 5-Dimethyle Aniline and dissolved it in Methanol, at first we mixed 0.75ml Methanol. Next we mixed 1.0ml, 1.25ml, 1.50ml, 1.75ml, 2.0ml Methanol respectively as solvent and changed the concentration of 2, 5-Dimethyle Aniline. For different concentration we measured the second harmonic response.
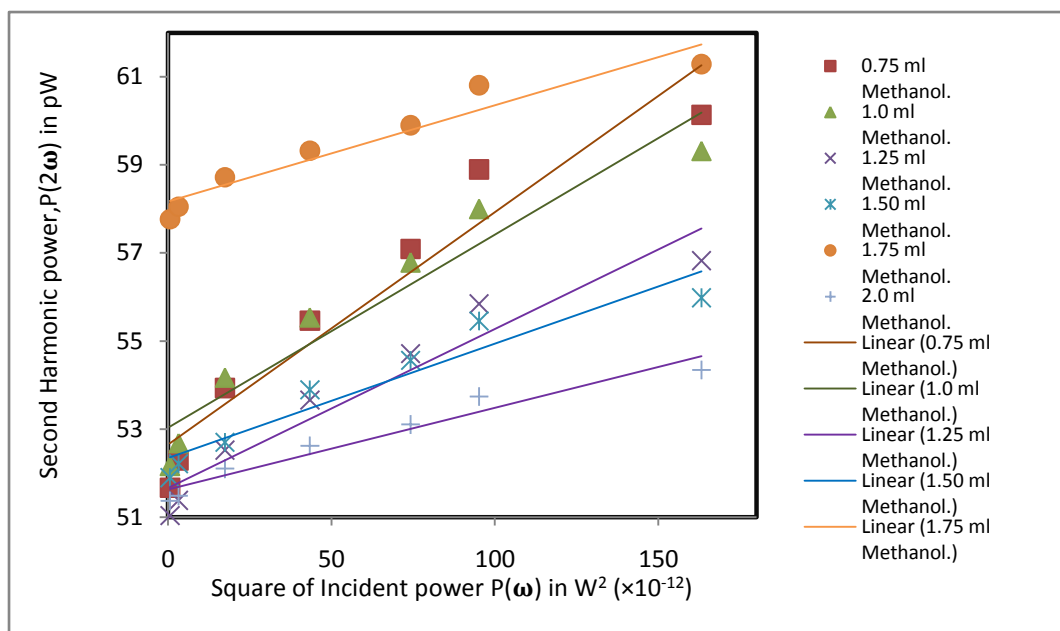
Figure 3: The second Harmonic power vs. Square of Incident power graph for different concentration of 2, 5-Dimethyle Aniline dissolved in Methanol.

## V.    RESULT

Table 7: Number Density of different concentration of 2, 5-Dimethyle Aniline and for each concentration the value of corresponding quadratic coefficients (q.c.)

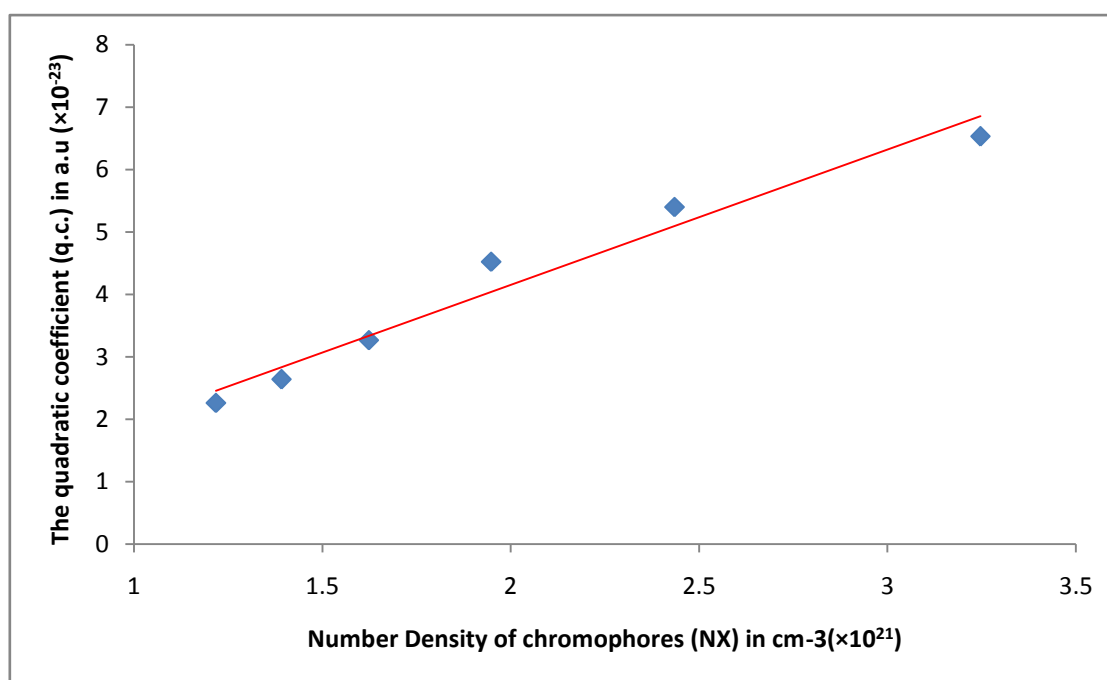| 0.5ml 2,5-Dimethyle Aniline dissolved in Methanol in ml. | Number Density ($N_X$) in $cm^{-3}$ | Quadratic Coefficients (q.c.) in a.u |
|---|---|---|
| 0.75ml | $3.247 \times 10^{21}$ | $6.530 \times 10^{-23}$ |
| 1.00ml | $2.435 \times 10^{21}$ | $5.399 \times 10^{-23}$ |
| 1.25 ml | $1.948 \times 10^{21}$ | $4.520 \times 10^{-23}$ |
| 1.50 ml | $1.624 \times 10^{21}$ | $3.265 \times 10^{-23}$ |
| 1.75 ml | $1.392 \times 10^{21}$ | $2.637 \times 10^{-23}$ |
| 2.00 ml | $1.217 \times 10^{21}$ | $2.260 \times 10^{-23}$ |



Figure 4: The Linear dependence between the quadratic coefficient (q.c.) and Number Density of the chromophores (x) graph are shown.

From the fig. (4) we get the value of the intercept, $b_0$ =0.184×$10^{-23}$a.u and the value of slope $b_1$=2.168×$10^{-44}$(a.u ×$cm^3$). We know the value of Number Density of Methanol ($N_X$) is 1.487×$10^{22} cm^{-3}$ and first hyperpolarizability $(\beta_{HRS})_S$ of Methanol is (0.69±0.07) ×$10^{-30}$ esu. Using equation () the $< \beta_{HRS}^2 >_X$ value of 2, 5-Dimethyle Aniline is

$$< \beta_{HRS}^2 >_X = \frac{2.168 \times 10^{-44} \text{ a.u} \times cm^3}{0.184 \times 10^{-23} \text{a.u}} \times 1.487 \times 10^{22} \, cm^{-3} \times (0.69 \pm 0.07 \times 10^{-30} \text{ esu})^2$$

$$\therefore < \beta_{HRS} >_X = 9.1332 \times 10^{-30} \text{ esu.}$$

Using the Hyper-Rayleigh Scattering technique we found that the value of 2, 5-Dimethyle Aniline first hyper-polarizability $< \beta_{HRS} >_X$ is 9.1332× $10^{-30}$ esu.

## VI.    CONCLUSIONS

In conclusion, we report on the experimental investigation that the 2,5-dimethyleaniline shows large $\beta$(=9.1332× $10^{-30}$ esu.) values. The first hyper-polarizability ($\beta$) of 2,5-dimethyleaniline (DMA), dissolved in Methanol, was investigated by means of the Hyper-Rayleigh scattering technique utilizing the Internal Reference Method. Generation of incoherent optical second harmonic was observed and the experiments allowed the determination of large first order hyper-polarizability associated to the DMA. An Argon Ion Laser operating at 457 nm was used as the excitation source to generate the second harmonic scattered light. The calculated results indicated DMA has a potential for SHG device applications, owing to its remarkable $\beta$ value.

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